3.0 RECYCLING AND RECOVERY OF MATERIALS
FROM SOLID GaAs WASTES

Due to the economic value of gallium, a number of recovery methodologies have been developed and tested over the years, but none have been applied for in-plant pollution prevention. The first step in these processes is typically to separate the gallium and arsenic. A well-documented method to accomplish this separation is to contact the solid waste stream with an aqueous solution or a heated bath, allowing a chemical reaction to facilitate separation. These separation media consist either of an oxidizing species such as hydrogen peroxide [1-2] or nitric acid [3-6], or of molten sodium hydroxide.[7] Once in solution or the heated bath, the gallium is then sequentially removed using a number of additional methodologies. While these practices have been demonstrated as workable, they all involve the introduction of a very large volume of an additional media in order to effect separation. This larger-volume media then must itself be treated (e.g., to preclude the release of toxic arsenic or to recover gallium). Thus, rather than merely separating the constituent elements from one another, these approaches result in the requirement for further processing (for metal recovery) from a much larger waste stream.

3.1 CURRENT DISPOSAL/RECYCLING METHODOLOGY

On a material weight basis, approximately 50% of solid GaAs wastes generated by semiconductor foundries are currently disposed of, and 50% are treated off-site for recovery of the gallium fraction. Because GaAs is not (at this time) a listed hazardous waste, disposal usually implies that the waste materials are placed into 55-gallon barrels, and disposed of in landfills. When GaAs wastes are sent to the only existing U.S. recycler, only gallium is presently being recycled and arsenic is presently <u>not</u> recycled.

One major problem with the existing disposal approach is that GaAs may be converted to the insidious gaseous toxin arsine (AsH_3) under acidic conditions. (Arsine gas is immediately lethal in concentrations as low as 250 ppm; lower concentrations result in chronic effects. The LD_{50} for arsine is 0.5 ppm.) It is well documented that landfills are typically anaerobic (reducing), with the simultaneous formation of organic acids such as acetic and formic acids. Therefore, GaAs exposed to typical landfill conditions could theoretically be easily converted to arsine gas. Even under less catastrophic circumstances, such as the oxidation of the released arsenic to the trivalent or pentavalent state, aqueous-phase arsenic will still represent a measurable toxic threat.

The prevailing attitude within the GaAs bulk crystal industry is that the existing disposal <u>and</u> recycling approaches are satisfactory. Under existing U.S. environmental laws, the original GaAs crystal grower is liable for any future environmental cleanup costs related to releases of the arsenic into the environment, with or without recycling of the gallium from the waste stream. Perhaps the only reason why such costs have not begun to be incurred by today's crystal growers is because the industry is only approximately twenty years old, and so arsenic contamination that is directly attributable to GaAs production has not yet been observed. Judging from the large monetary sums currently being awarded to localities (for liabilities) and environmental contractors (for

cleanup) from disposal of arsenic-containing wood preservatives, it is safe to predict that the future holds some very unpleasant economic surprises for today's GaAs crystal growers if disposal approaches are not altered to allow for arsenic recovery and reuse. Therefore, recycling of both gallium and arsenic from GaAs manufacturing wastes offers both short-term (gallium recovery) and long-term (minimizing arsenic-related liabilities) economic benefits

3.2 RECOVERY PROCESS DEVELOPMENT

Thermal processing of GaAs solid wastes to recover gallium has also been demonstrated in the past. While thermal separation under air has been achieved for GaAs, that procedure results in the formation of arsenic and gallium oxides.[11,12] These oxide "slags" require an additional processing step (reduction) to obtain reusable metals. Therefore, from an in-plant pollution prevention approach, separating under an inert atmosphere or under vacuum is more desirable in order to minimize the number of processing steps (and thus the overall cost of the recovery operation). This too has been attempted, and many of the processes described are very exact with respect to necessary conditions to achieve thermal separation.

Initial studies of the effects of high temperature conditions (above 950°C) showed that thermal cracking of the GaAs takes place until the partial pressure of arsenic vapor in the head space prevents further sublimation of arsenic. Thus, a conceptual process was proposed in which the GaAs solids would be subjected to high temperatures at reduced pressure with a continual draw-off of released arsenic vapors. Continued operation of such a process would ultimately result in removal of most of the arsenic leaving a residue that would be high in gallium, and which would contain any unmelted (or high-boiling) contaminants. However, it was expected that such thermal separation alone would not produce gallium or arsenic products of sufficient purity for reuse in semiconductor crystal growth. Further processing steps would be required whereby the arsenic-rich vapors and the gallium-rich residue could be further purified to acceptable levels for reuse.

3.2.1 Purification Thermodynamics of Arsenic

Processes for recovery and purification arsenic are not as well developed as those proposed for gallium. In fact, no recovery/purification of arsenic is attempted in any of the gallium arsenide recovery processes. This is the case in all reported thermal separations - liquid gallium is recovered, but condensed arsenic is disposed of, presumably due to its low raw material cost.[8-12]

Arsenic purification has been achieved through the zone refining of such arsenic compounds as arsenic trioxide,[13,14] arsenic trichloride,[15] or arsine gas,[16] followed by reduction to the elemental state with a number of reducing agents, including hydrogen[17,18] or metallic species such as aluminum and calcium.[14] Arsenic has also been purified through a zone refining process whereby the arsenic is heated to 814°C at a pressure of 36 atmospheres, so as to achieve a solid-liquid transition.[19] Using any of these concepts within a GaAs recovery process would mean that the compound purification processes

would require three processing steps (conversion of elemental arsenic to a compound, followed by purification and then re-reduction to the elemental state). Such an approach also would present inherent toxicity concerns (since the only truly successful reduction is that using hydrogen gas, of which arsine is a thermodynamically-feasible byproduct). The high-pressure approach to arsenic purification also bears significant hazards for in-house recovery operations.

Purification of arsenic using sublimation mechanisms has been achieved in the past,[20,21,22,23] and because it is a one-step process with minimal energy or toxicity (only metallic arsenic is involved and not the more toxic oxides or hydrides) concerns, this approach was chosen for incorporation into the overall recovery scheme. The prior art suggests that the use of an inert carrier gas (e.g., nitrogen) aids in the separation of arsenic from impurities.

3.2.2 Purification Thermodynamics of Gallium

Gallium purification requires a significantly different purification methodology than those traditionally applied to other semiconductor materials (e.g. silicon or germanium) because gallium is present in the liquid phase at ambient temperatures and pressures. For this reason, gallium purification has been attempted in a multitude of fashions. The methodology that was used for a number of years involved the conversion of (impure) gallium to gallium trichloride (which is a solid), followed by zone refining of the gallium trichloride, and reduction to pure metallic gallium.[24-30] This methodology was not considered further for our recycling process because, like arsenic purification utilizing arsenic trichloride, it is a three-step process which requires material addition. Additional purification methodologies that were rejected because they involve a three-step purification process included electrolysis,[31-33] hydride reduction,[34] and nitride separation.[35] A one-step physical separation process of gallium from its impurities was desired.

Because gallium has a large liquidus range (b.p. = 2403°C), a considerable amount of energy would be required to separate gallium from other metals and from refractories (e.g. diamond) utilizing a liquid-vapor separation methodology. Therefore, a separation based on liquid-solid phase transitions is required, of which three procedures are documented in the literature: single crystal lifting process, fractional crystallization, and zone melting. The single crystal lifting process achieves purification by contacting a seed crystal with a gallium melt, with gradual lifting,[36,37] but due to its low productivity, this physical separation methodology was rejected. Fractional crystallization exhibits a similarly low productivity and was also rejected.

Zone melting of gallium appears to offer a reasonable and cost effective method for purification of gallium from a thermal separation process, provided that the initial separation results in a gallium-rich stream that is better than 90% pure gallium. At such a purity level, the gallium-rich product should have a melting point close to the melting point of pure gallium (approximately 35°C). Under such conditions, the gallium-rich product would be a solid at room temperature and a low-energy heat source could easily

raise the product temperature to the melting point allowing for an inexpensive zone refining operation.

3.3 PROTOTYPE SYSTEM

Based on the initial studies, a conceptual recovery process was developed that could conceivably be operable in a small space and at reasonable costs. The proposed process also seemed likely to achieve product purities sufficient to recycle the recovered materials back into the semiconductor crystal growing operation. The process was envisioned to include an initial thermal separation of GaAs into an arsenic-rich vapor stream and a gallium-rich residue. These product streams would then undergo further processing for purification to necessary levels.

A major result of the research performed under the subject grant has been the development of a three unit operation procedure in which the solid wastes are thermally separated into their constituent elements (with a minimum of energy input or additional handling). Then each of the separated elements (gallium and arsenic) is purified to the required levels for further crystal growth. Prior work with GaAs thermal separation and constituent element purification provided a template for the development of this "optimum process", and subsequent thermodynamic consideration of each of these unit operations provided a theoretical basis for implementation into the developed process.

Figure 3.1 shows a schematic of the developed process for solid III-V materials as it currently exists. As a result of this research, it is now known that the lowest cost means
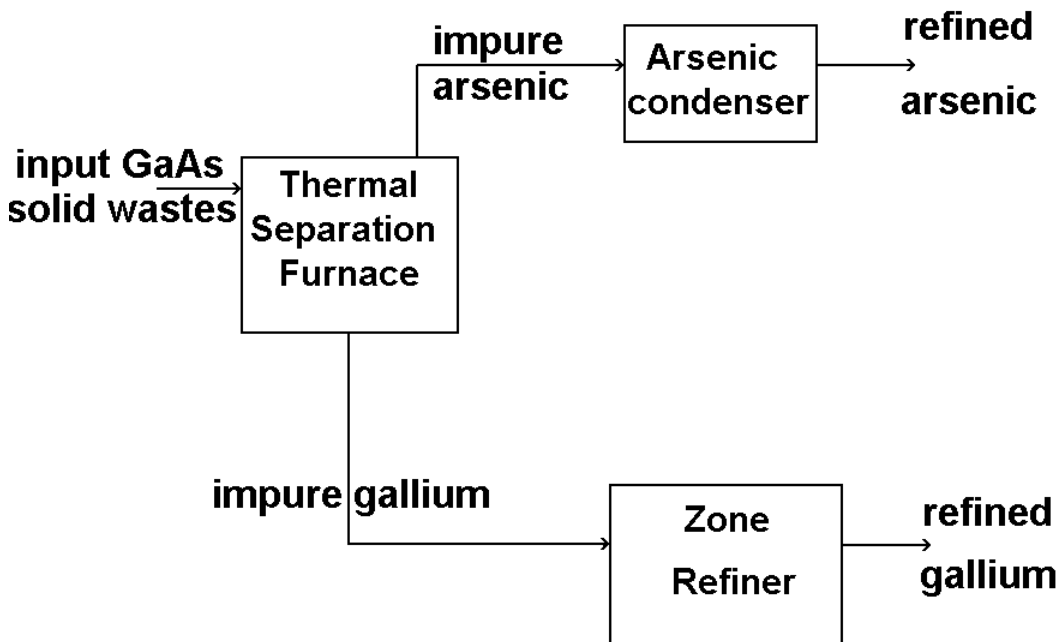

Figure 3.1 - Schematic of the Recovery Process for III-V Solid Wastes

21

to separate III-V solids is through the low-pressure, high-temperature process shown as the first unit operation in Figure 3.1. It is also now known that some further processing of recovered gallium or arsenic is necessary in order to <u>maximize</u> the quantity of recovered material for reuse.

<u>3.3.1 Unit Operation 1 – Thermal Separator</u>

The first and most critical operation in the developed recovery process is the thermal separation furnace. Figure 3.2 shows a cross-section of the thermal separation furnace that was constructed for laboratory and field trials of the proposed concept. The unit can be operated at temperatures above 950°C and at reduced pressure with an inert atmosphere. The off-gases are continually pumped through a series of condensers for capture of the arsenic-rich vapors. The residue in the reactor contains the gallium-rich fraction mixed with a separable slag of other contaminants.

It was known that thermal separation alone could not achieve product purities great enough to allow for immediate reuse of the recovered products. In addition to contaminants introduced into the waste stream, some contaminants could be intentionally introduced into the crystals as dopants for specific control of the crystal's electronic characteristics. Dopants commonly found in GaAs include Si, Zn, and C or Cr. These dopants typically occur in concentrations of about 10^{18} atoms/cc.   Some of these dopants (e.g., C at about 10^{15} atoms/cc) are utilized to make GaAs semi-insulating, and some are utilized to make GaAs semiconducting n-type (Si) or p-type (Zn). The physical characteristics of each dopant are important because they will dictate where the dopant
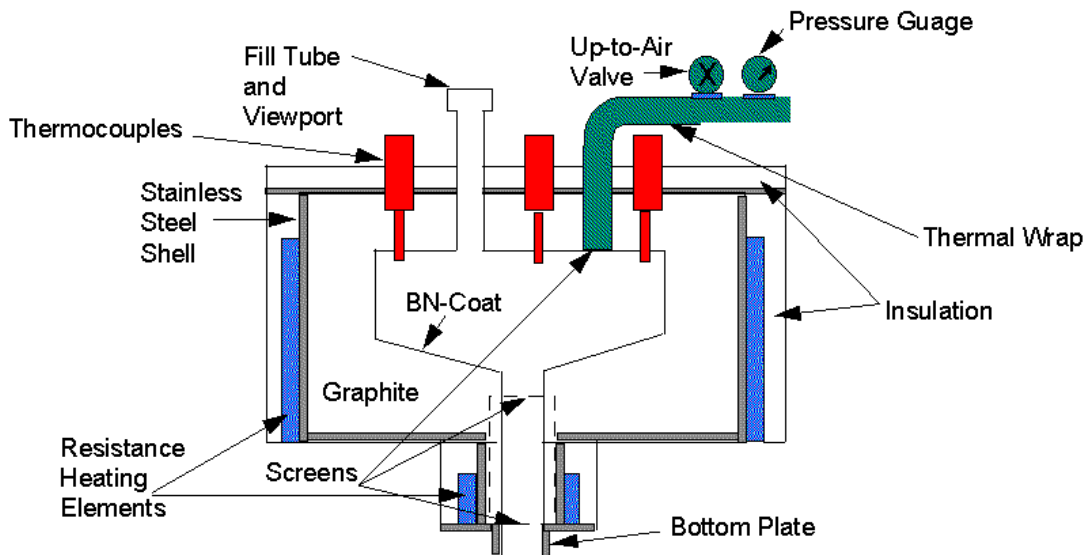

Figure 3.2 Cross-section of Unit Operation 1 – Thermal Separation Furnace

will likely occur in the product streams resultant from the thermal separation. For example, silicon and iron are very soluble in liquid gallium, and so these elements can be expected to remain with the gallium, forming an impure "slag". Simultaneously, "volatile" dopants such as sulfur and selenium are expected to partition into the arsenic fraction. For this reason, further processing steps were incorporated into the process for purification of the gallium-rich and arsenic-rich product streams.

3.3.2 Unit Operation 2 - Low-Temperature Zone Refining of Gallium

Because the impurity levels in the product gallium from doped GaAs sources are expected to be fairly low (because dopant concentrations are relatively low), then the melting temperature of the "impure" gallium should approach that of pure gallium (i.e., ~ 35°C.) UDRI has developed a system for the purification of nearly pure gallium with small concentrations of impurities (Figure 3.3). Specifically, it involves chilling the gallium with ice water or refrigerant to 0°C or less, and then using a controlled heat
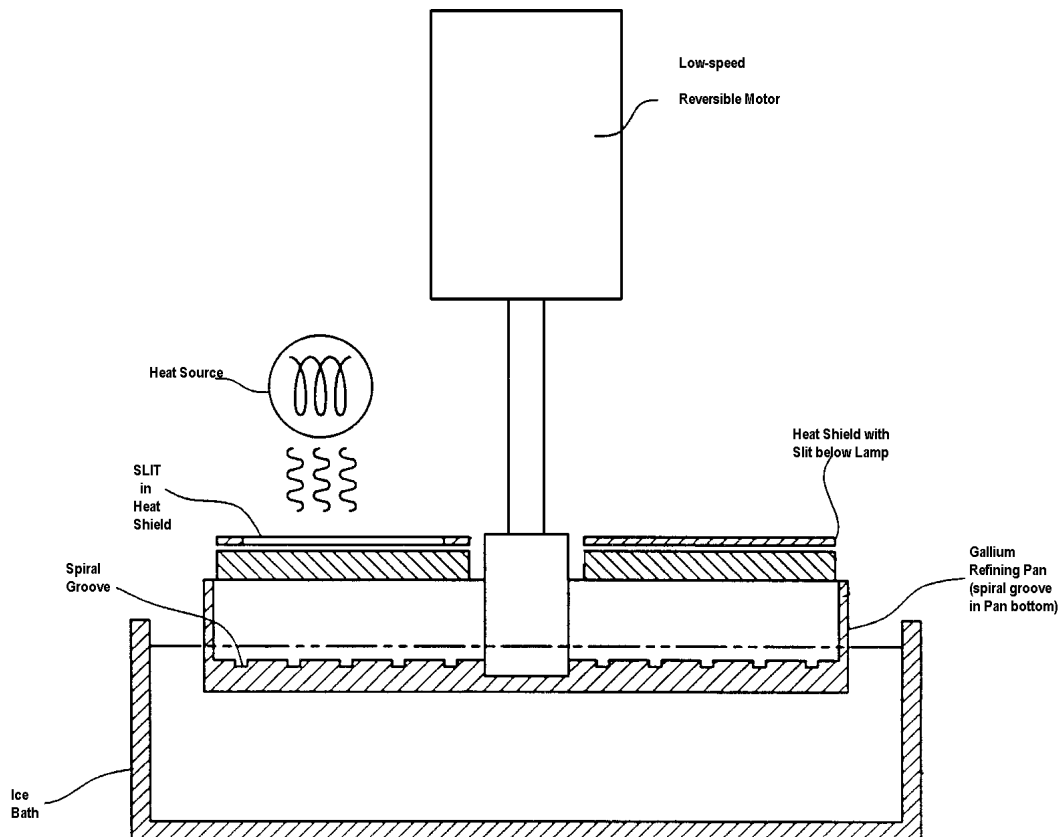

Figure 3.3 - Schematic of Existing Equipment for Low-Temperature Purification of Gallium

source (heat lamp) to heat specific zones of the gallium sample. (Note: Although gallium is a solid at ambient temperatures of 20-25°C, this is not a sufficiently cold temperature for efficient zone refining due to supercooling effects. In other words, zone refining from ambient room temperature will not be successful because the temperature difference between solid and liquid will not be sufficient to effect impurity segregation.) The molten zone is allowed to pass through the gallium by slowly rotating the pan containing the gallium. Based upon the segregation coefficients of each of the contained "impurities", the dopant elements will segregate to both ends of the spiral groove in the gallium refining pan shown in Figure 3.3 and can then be removed.

3.3.3 Unit Operation 3 - Sublimation Refining of Arsenic

As noted previously, the arsenic fraction can be contaminated with the more volatile dopants, especially carbon. UDRI has achieved some purification of arsenic through the use of a repeated sublimation/condensation process as is shown in Figure 3.4. Specifically, the arsenic in the first condenser (e.g. evolved from the low-pressure, high-temperature process in Figure 3.2) is heated to slightly above the sublimation temperature of arsenic (610°C) in an inert gas stream such as nitrogen, and recondensed in a second condenser. This thermally separates the arsenic from impurities due to differences in partial pressure and volatility. Further processing can be achieved through additional sublimation/condensation (e.g., heating from condenser 2 into condenser 3, etc.).
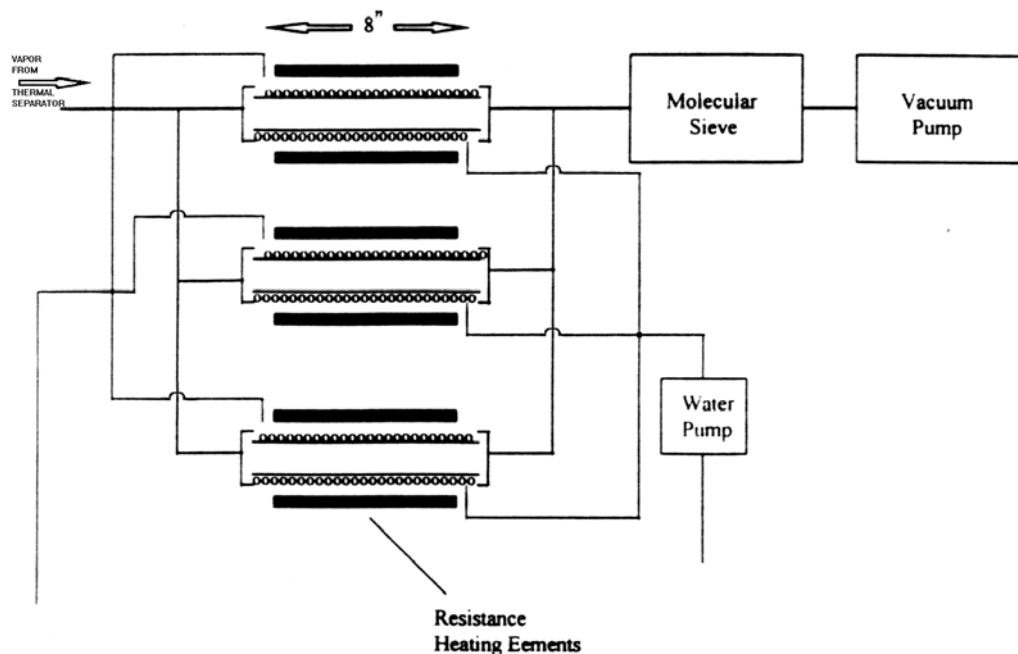

Figure 3.4 - Schematic of Existing Equipment for Sublimation /Purification of Arsenic

<u>3.3.4 Analytical Results</u>

        Initial studies were performed to evaluate the basic thermal separation concept
that ultimately was incorporated as unit operation number 1 in the concept process.
Analyses of samples were conducted using Energy Dispersive Spectroscopy (EDS). This
surface analysis technique is capable of detecting the presence of atomic constituents in
solid samples down to the parts per million (ppm) level. Thus, EDS will show the
presence of unacceptable contaminants at the ppm level and was suitable for initial
assessments of the performance of the recovery processes. However, EDS is not a truly
quantitative technique and it was known that a more sensitive technique would ultimately
be required in order to demonstrate that the recovered material has sufficient purity for
reuse.

        Figure 3.5 shows an EDS analysis of a slab of unreacted GaAs solid waste typical
of the feed material used in subsequent studies. Initial studies of the thermal separation
concept were performed under an inert atmosphere (N_2) but at atmospheric pressure. It
was soon realized that as the sample released volatile arsenic, the partial pressure of
arsenic rose until further arsenic sublimation stopped. Continued operation at high
temperature allowed other, less-volatile materials to escape with no real increase in the
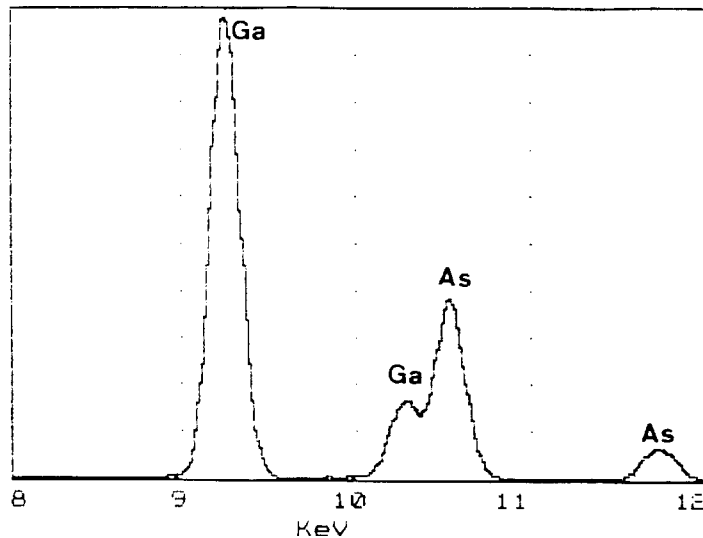arsenic removal

Figure 3.5 EDS Analysis of Unreacted GaAs

rate. Figure 3.6 shows the EDS analysis of a recondensed solid sample of the volatile
fraction resulting from a 30 minute run at approximately 1000°C. The presence of an
indium peak results from a low-level ($< 0.3\%$) of indium dopant present in the original
material. Figure 3.7 shows that, for such operating conditions, high levels of arsenic
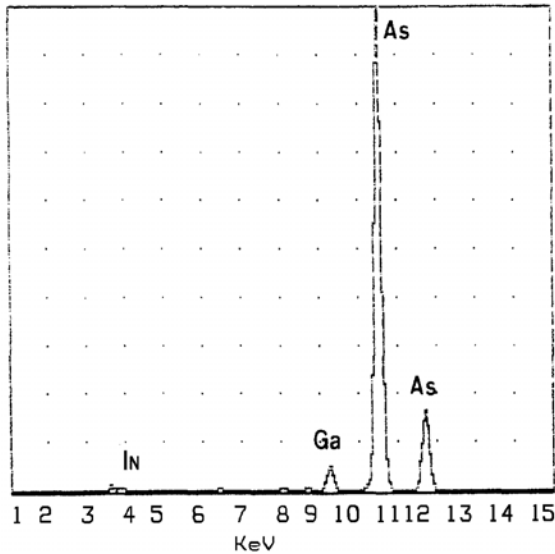remain in the residues. In fact, continued operation at high temperature and at
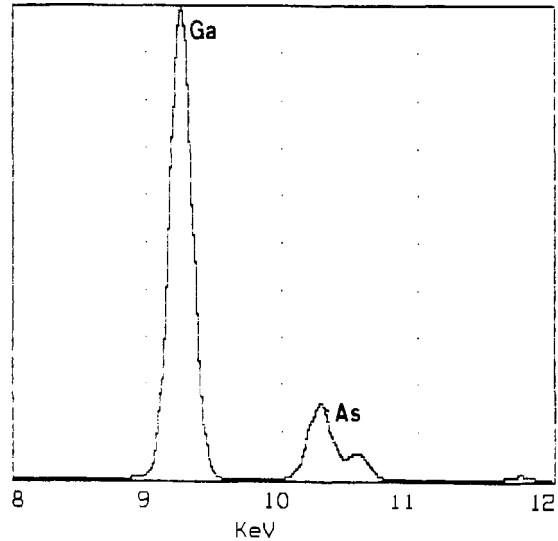
Figure 3.6 EDS Analysis of Volatiized Material

Figure 3.7 EDS Analysis of Residue

atmospheric pressure and above can result in the eventual volatilization of gallium so that the recondensed solid will contain significant proportions of gallium as a contaminant in the arsenic-rich fraction (Figure 3.8).
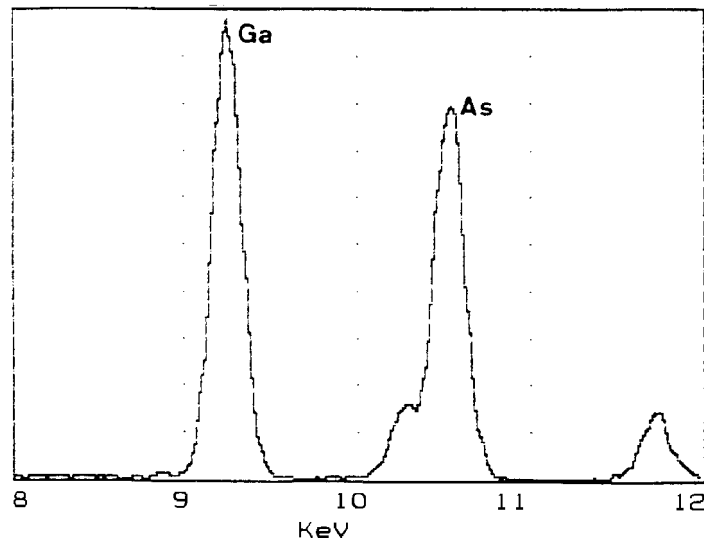

Figure 3.8 EDS Analysis of Volatile Material after 2-hour Run

At this point, it became obvious that, for the process to achieve effective separation of the gallium and arsenic fractions, the evolved arsenic must be continuously removed and recondensed outside of the thermal separation reactor. A thermal reactor was developed that could be continuously evacuated through condenser units for capture of the evolved arsenic. The EDS analysis results on the residual solids are shown in

26

Figures 3.9 and 3.10 for two runs wherein the evolved gases were pumped out through cooled condensers. In each of these samples, some low level of unvolatilized arsenic is shown (the small "knee" to the right of the smaller gallium peaks in each figure) indicating that the gallium-rich residue would probably still require further purification.
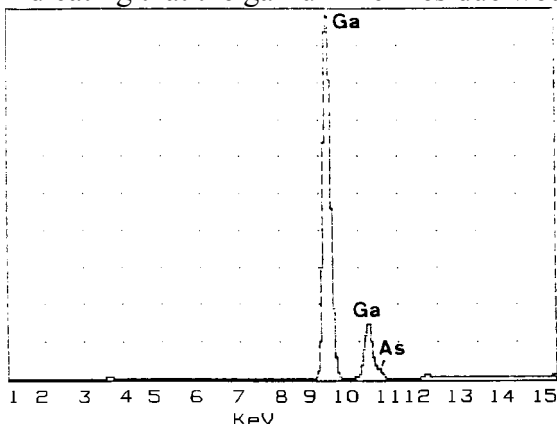

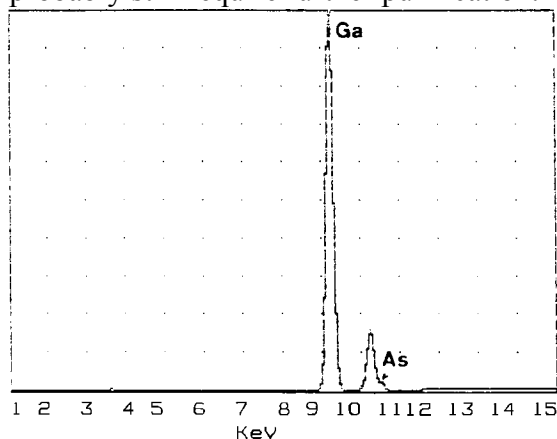**Figure 3.9 Analysis of Residue from 1-hour Run with Continuous Evacuation**

Figure 3.10 Analysis of Residue from 2-hour Run with Continuous Evacuation

Because of the presence of the low levels of arsenic (approximately 3 to 4%) in the residue after thermal separation, it was decided that an additional process step would be required to achieve adequate gallium purity for its reuse. Thus, a low-temperature zone refiner was chosen as the probable best method for purification of the residual gallium-rich material. Similarly, because the volatile fraction could contain materials other than arsenic, it was decided that a sequence of condensation steps followed by volatilization steps would purify the arsenic-rich fraction evolved in the original thermal separation. That logic resulted in the development of the concept process shown in Figure 3.1 at the beginning of this section.

2.3.5 Field Trials at a Semiconductor Foundry

The process for recovering reusable materials from solid GaAs wastes was tested at the AXT Fremont facility in August of 1996. While the primary goal of the field testing was to establish that the proposed recovery process could be effected without disturbing normal GaAs foundry operations, a secondary objective was to establish the purity of the recycled materials.

Waste GaAs kerf and wafer pieces were subjected to the low-pressure, low-temperature thermal process utilized as the first unit operation in the recovery process for solids. Specifically, batches of waste material were placed into a graphite/SiC crucible within the recovery reactor, the pressure reduced to < 1 torr, and the temperature raised to > 1050°C. The waste material was processed for 2-3 hours under these conditions, and arsenic separated out as a condensable vapor, leaving a gallium-rich residue in the crucible. The arsenic and gallium fractions were collected and it was seen that the residue was composed of two different gallium-rich fractions. The purity of the two different gallium fractions from this process is shown in Figures 3.11 and 3.12 which

present SIMS (Secondary Ion Mass Spectrograph) analyses of the product streams. Figure 3.11 is a SIMS analysis of a low-melting fraction that results from this first unit operation. As can be seen, the resultant material is virtually pure gallium. Figure 3.12 shows the purity of a higher-melting "slag" that typically forms around this pure gallium. As can be seen, this material contains substantial amounts of iron, silicon, and other detrimental elements, which account for the higher melting temperature of this fraction.

Equivalent quantities of arsenic were recovered from the condenser as a finely divided powder. No reliable method of measuring the purity of arsenic to the four-9s level was available for the study. The only reliable method to measure the purity of recovered arsenic, is by using it in combination with gallium of certified purity to grow crystals of gallium arsenide. The purity of the recovered arsenic can then be determined by measuring the characteristics of these crystals.

Because of the extremely hjigh purity of the gallium fraction and the difficulties of measuring arsenic purity, the arsenic purification step and the gallium zone refining step were not performed during the field test of the process. Discussions with the foundry operator indicated their desire to participate in future development activities aimed at a commercial process for in-plant pollution prevention.
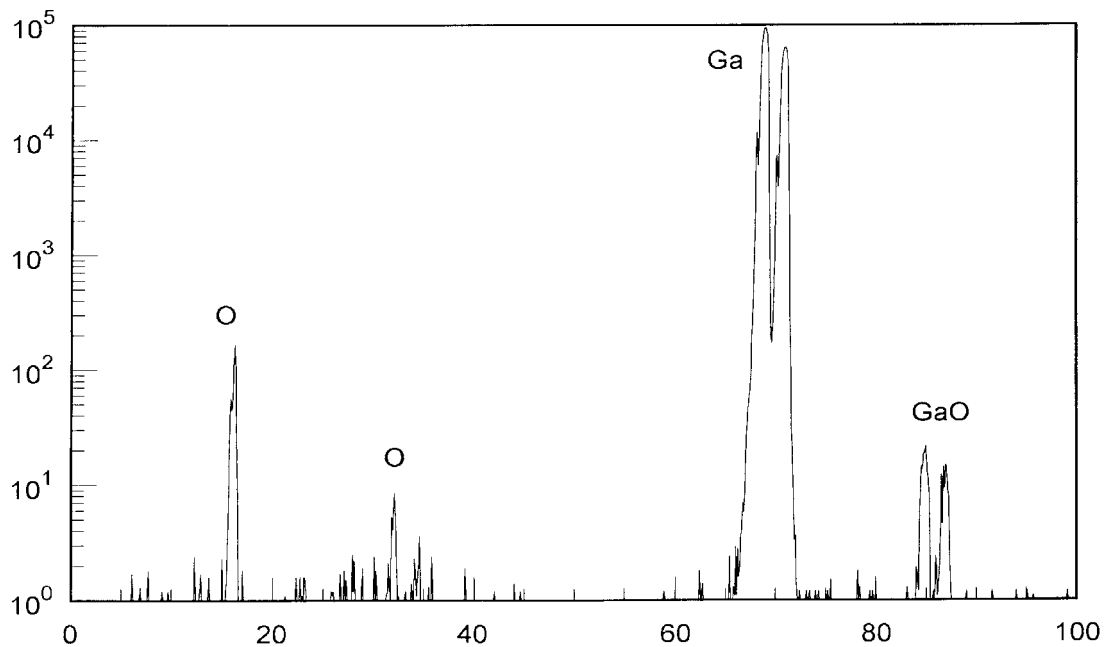

Figure3.11 - SIMS Analysis of Pure Gallium Fraction Resulting from Thermal, Low-Pressure Recovery of GaAs
(note - presence of oxygen and GaO peaks results from use of
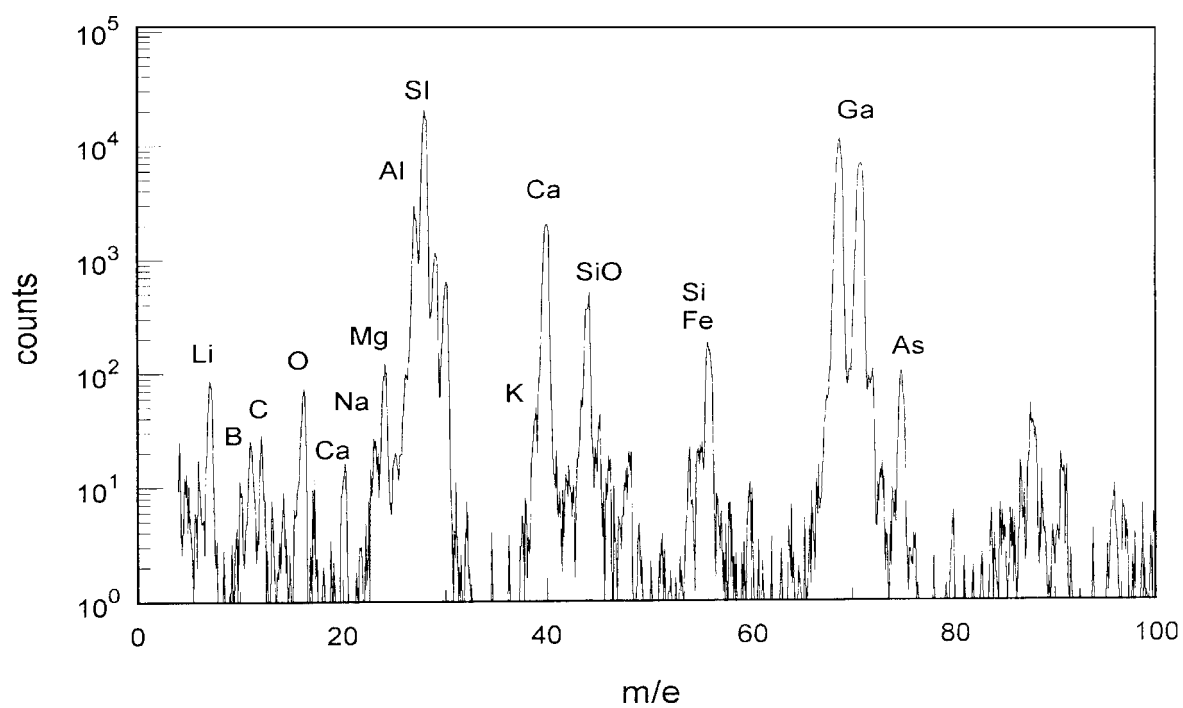oxygen as primary ion source)

Figure 3.12 - SIMS Analysis of Gallium "Slag" Resulting from Thermal, Low-Pressure Recovery of GaAs